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(54) Title: METHOD FOR THE ADHESION OF FLUORINATED RESINS TO METALS			
(57) Abstract The objective of the present invention is to offer a method for improving the adhesion of fluorinated resins to metal materials, and for obtaining composite materials of metal materials and polyvinylidene fluoride resins. A metal-adhesive fluorinated composition can be used as an adhesive agent between the fluorinated resins and the metals or can replace the fluorinated resins.			

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Specification

METHOD FOR THE ADHESION OF FLUORINATED RESINS TO METALS

TECHNICAL FIELD OF THE INVENTION

5 The present invention relates to a method for the adhesion/lamination of fluorinated resins and metals which are inherently non-adhesive thereto, and the invention can be applied to steel pipe linings, chemical plant components, and binders for the electrodes of batteries, etc, where corrosion resistance, weathering resistance or chemical resistance is demanded.

PRIOR ART

10 As a fluoropolymer of outstanding weatherability and chemical resistance, etc, which can be melted and moulded, polyvinylidene fluoride (hereinafter abbreviated to PVDF) resin is used for coating materials and for electrical/electronic components, steel pipe linings, chemical plant components and weather-resistant/stain-resistant film, etc. However, since it has practically no adhesion properties in terms of other
15 materials, it suffers from the problem that it is difficult to modify or composite with other materials.

Hence, the mixing of other polymers with PVDF has been attempted in order to overcome this disadvantage, but there are few polymers having adhesion properties or compatibility in respect of PVDF, and because of adverse effects on the physical
20 properties of the PVDF, etc, the application range is extremely restricted. For example, polymethyl methacrylate resin (hereinafter abbreviated to PMMA) is known to be a material with good compatibility for PVDF (JP 43-12012 and JP51-18197), but the glass transition temperature of PMMA is very high when compared to that of PVDF, so mixtures of these lack flexibility and they have poor adhesion to metals.
25 On the other hand, composites with polycarbonate (JP57-8244), composites with modified polyolefins having functional groups (JP62-57448), and composites with polyimides (JP2-308856), and the like, have also been proposed, but these combinations are lacking in compatibility and they are inferior in terms of their adhesion to metals. In addition, composites with acrylate or methacrylate elastomers
30 have also been proposed (JP4-218552), but nothing is known of the adhesion to metals system.

PROBLEM TO BE RESOLVED BY THE INVENTION

The present invention has the objective of improving the adhesion of fluorinated resins to metal materials, and of offering a method for obtaining
35 composite materials of metal materials and fluorinated resins.

CONFIRMATION COPY

MEANS FOR RESOLVING THE PROBLEM

The present inventors have found that a fluorinated composition comprising at least 2 of the 3 following components :

- (a) at least a PVDF resin,
- 5 (b) at least a acrylic an/or methacrylic polymer having functional groups with bonding properties or affinity in respect of metals,
- (c) at least a vinylidene fluoride copolymer resin

exhibits good adhesion properties on metal materials, and they have discovered that such characteristics are effective in the production of composite
10 materials comprising such compositions and metals.

The PVDF resins (a) referred to here can be selected from polyvinylidene fluoride homopolymers and have preferably a melt flow rate (MFR) of 0.01 to 300 g/10min at 230 °C under a load of 2.16 kg.

The vinylidene fluoride copolymers (c) are copolymers of vinylidene fluoride
15 (VF2) and other monomer(s) which can copolymerize with VF2, and the percentage VF2 component in these copolymers should be from 50 to 95 wt%, more preferably from 75 to 95 wt%. As the copolymerizable other monomer here, fluoro-monomers such as tetrafluoroethylene, hexafluoropropylene, tri-fluoroethylene and trifluorochloroethylene, etc, are preferred, and it is possible to use one or more of
20 these. It is desirable that the copolymers (c) have a room temperature flexural modulus of no more than 1.000 MPa and that they exhibit a breaking elongation of at least 50% and preferably a melt flow rate (MFR) at 230°C under a 2.16kg load in the range from 0.01 to 300g/10 min.

The fluorinated resins (a) and (c) may be obtained by the polymerization of
25 vinylidene fluoride monomer or vinylidene fluoride monomer and other monomer(s) by the suspension polymerization method or emulsion polymerization method, etc,

The acrylic and/or methacrylic polymers (b) are polymers in which the chief component is an alkyl acrylate and/or alkyl methacrylate and which has, in the main chain, in the side chains or at the terminals, functional groups which exhibit bonding
30 properties or affinity in terms of metals. As examples of such polymers, there are the random copolymers, block copolymers and graft polymers produced by methods such as radical polymerization, ionic polymerization or co-ordination polymerization from at least one type of monomer selected from alkyl acrylates and alkyl methacrylates, plus monomer with a functional group which exhibits bonding
35 properti s or affinity in respect of metals.

As examples of functional groups which exhibit bonding properti s or affinity in respect of metals, there can be cited carboxylic acid groups or carboxylic acid

anhydride groups, epoxy groups (glycidyl groups), mercapto groups, sulphide groups, oxazoline groups, phenolic groups, ester groups, and the like.

One example of the aforesaid acrylic and/or methacrylic polymer comprises the copolymer of monomer with a carboxylic acid group or carboxylic acid anhydride group and an alkyl acrylate and/or alkyl methacrylate. In such circumstances, specific examples of the alkyl (meth)acrylate are methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate. Further, as specific examples of the monomer with a carboxylic acid group or carboxylic acid anhydride group, there are acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid, alkenylsuccinic acid, acrylamido-glycolic acid, allyl 1,2-cyclohexanedicarboxylate and other such unsaturated carboxylic acids, and maleic anhydride, alkenylsuccinic anhydride and other such unsaturated carboxylic acid anhydrides, etc.

Further, it is preferred that at least 50 wt%, and more desirably at least 70 wt%, of this acrylic and/or methacrylic polymer be composed of at least one type of monomer selected from acrylate and/or methacrylate esters. The amount of the contained functional groups which exhibit bonding properties or affinity in respect of metals will preferably be from 0.01 to 2 mole per 1kg of the acrylic and/or methacrylic polymer. In the case where this polymer component is a copolymer of at least one monomer selected from acrylate and/or methacrylate esters and monomer having a carboxylic acid group or carboxylic acid anhydride group, the proportion of the monomer with a carboxylic acid group or carboxylic acid anhydride group will preferably be from 0.2 to 30 wt% of the said copolymer, and more preferably from 1 to 20 wt%. Further, as a constituent component, there may also be included in the molecular chain, besides the above, vinyl monomer such as styrene or modified units such as imides, but the amount of these will not be more than 50 wt%, and preferably not more than 30 wt% of the said polymer.

- When the metal-adhesive composition contains (a), (b) and (c) components, it contains from 0.5 to 100 parts by weight of an acrylic and/or methacrylic polymer (b), from 1 to 200 parts by weight of vinylidene fluoride copolymer resin (c) per 100 parts by weight of polyvinylidene fluoride resin (a).

The metal-adhesive composition of the present invention can be prepared by a solution process or melt process. In the case of a solution process, the aforesaid components (a), (b) and (c) may be dissolved in the prescribed proportions in a solvent such as N-methylpyrrolidone, N,N-dimethylformamide, tetrahydrofuran, dimethyl-acetamide, dimethylsulphoxide, hexamethylphosphoramide, tetramethylurea, acetone, methyl thyl ketone or the like, at a temperature lower

than the boiling point of the solvent used. In the case of a melt process, production can be carried out by a conventional method, i.e. heating and mixing the components (a), (b), (c) in the prescribed proportions using a screw mixing machine. Here, conventionally-known methods can be used as the method of melting and mixing, such as a Banbury mixer, rubber mill or single or twin-screw extruder, etc, and normally the resin composition is obtained by melting and mixing at 100 to 300°C and preferably, although it will also depend on the composition, 150 to 260°C.

In the present invention, if the amount of the vinylidene fluoride copolymer added per 100 parts by weight of the vinylidene fluoride resin is from 1 to 10 parts by weight, and preferably from 1 to 5 parts by weight, and, similarly, if the amount of the acrylic or methacrylic polymer is from 0.5 to 10 parts by weight, preferably from 1 to 5 parts by weight, then it is possible to improve the adhesion to metals without greatly altering the properties of the vinylidene fluoride resin. This method is especially effective where the adhesion process is a solution application method.

Further, this fluorinated composition of the present invention, the metal adhesion properties of which are improved by the aforesaid method, can be employed as the adhesive agent when sticking fluorinated resins to metals. In particular, in the case where the adhesion process is a melt process, it is preferred that the three component-composition is composed of 5 to 100 parts by weight of the acrylic or methacrylic polymer (b) with bonding properties or affinity in terms of metals and from 10 to 200 parts by weight of vinylidene fluoride copolymer (c) per 100 parts by weight of PVDF resin (a).

In the present invention, the fluorinated composition with improved metal adhesion can be used as an adhesive agent when sticking a fluorinated resin to a metal, the said fluorinated resin does not necessarily have to be composed of the same fluorinated resin as fluorinated resin which constitutes the surface layer. There can be selected, as the fluorinated resin employed in the adhesive layer, a resin having an appropriate melt flow rate (MFR), copolymer composition and melting point, according to the adhesion/processing operation.

As examples of the metal materials employed as the adhered base material in the present invention, there are iron, stainless steel, aluminium, copper, nickel, titanium, lead, silver, chromium, and alloys of various kinds, etc, and the form thereof is not particularly restricted.

EFFECTS OF THE INVENTION

As explained above, by means of the present invention it becomes possible to easily improve the adhesion of fluorinated resins (and of fluorinated resin-containing materials) and metal materials, and to easily obtain metal-adhesive fluorinated composite materials. The metal-adhesive fluorinated composite materials obtained by this method consist of fluorinated resin such as an extrusion moulded article (film, sheet, plate, pipe, rod, profile extruded article, strand, monofilament, fibre, etc), injection moulded article or press moulded article, etc, part or the entire face of which comprises a layer of the aforesaid metal-adhesive composition, and it is not especially restricted. Means for the preparation thereof include calendering, coextrusion, extrusion lamination, multi-layer injection, fluid immersion coating, dipping, spraying and coating the surface of a moulded body, etc. Here, the polyvinylidene fluoride resin used as the base material and the polyvinylidene resin used in the metal-adhesive composition may be the same or different.

The method of the present invention can be used for fluoro-coating materials employing fluorinated resin dissolved or dispersed in a solvent or for electric wire coating by means of fluorinated resin. Moreover, it can be used for the binders for the electrodes of lithium batteries, etc, and in such circumstances it is useful in improving the adhesion between the metal substrate (in the case of a battery, the current collector) and the electrode active material layer.

The method of the present invention for sticking fluorinated resins and particularly PVDF resins and/or VF2 copolymer resins to metals can be employed in various products, and it is valuable in many fields such as structural components of equipment where chemical inactivity is demanded in the chemical, pharmaceutical and foodstuffs industries, and exterior building materials and industrial materials where weatherability over a prolonged period is required, and also for the binders for electrodes in lithium batteries, etc.

For the electrode production process of lithium-ion batteries, it is useful to strengthen the adhesion between the metal substrate of the current collector and the electrodes' active material layer.

There is a great demand for smaller rechargeable batteries possessing high capacity and long life in portable electronic products (cellular phones, pagers, personal digital assistants, equipment for personal communication services, hand-held and laptop computers, video games, cam recorders, etc, electric vehicles. The lithium-ion batteries (LIBs) are an excellent solution because they are thin and lightweight, do not contain heavy metals than cause environmental problems and they provide higher energy density than existing nickel-cadmium, nickel-metal hydride, and lead-acid batteries.

The lithium-ion battery's laminate structure is generally as follows :

- a metal collector
- a lithium/metal oxide-based positive electrode or cathode,
- an electrolyte,
- 5 - a carbon-based negative electrode or anode ,
- a metal collector

The anode active substance can be made of any material which permits doping and releasing of lithium ions and is generally made of carbonaceous materials including cokes such as petroleum cokes and carbon cokes, carbon blacks such as
10 acetylene black, graphite, fibrous carbon, activated carbon, carbon fibers and sintered articles obtained from organic high polymers by burning the organic high polymer in non-oxidation atmosphere. Copper oxide or other electro-conductive materials also can be incorporated or added to the cathode active substance.

The binder which must possess high resistance to solvents and chemicals is
15 generally based on fluorinated resins, polyolefins, synthetic rubbers but fluorinated resins are preferred. The contents of fluorinated resins in the binder is preferably more than 90 wt%.

The PVDF resins are preferably used and more particularly these ones with more than 75 wt% VF2 because of their high resistance to solvents and to active
20 chemicals so as their high solubility in methylpyrrolidone which is a common solvent of lithium-ion batteries. Among PVDF resins, these ones consisting of mixtures of homopolymer of vinylidenefluoride and fluorinated copolymer(s), the contents of VF2 of the fluorinated copolymer(s) is 50 to 95 wt% and whose amount of homopolymer of vinylidenefluoride in the mixture is 50 to 99.5 wt% are also preferred.

25 An usual process for making the anode consists of mixing the carbonaceous material in powder form with a suitable amount of binder and is kneaded with a solvent to prepare a paste or slurry. Then a collector (generally copper) is coated onto the paste and is then dried and compacted to obtain the anode.

The lithium-ion battery cathode is generally made of lithium and oxide of
30 transition metals as manganese oxide and vanadium oxide, sulfides of transition metals such as iron sulfide and titanium sulfide, or composite compounds between these substances as composite oxides of lithium and cobalt, composite oxides of lithium, cobalt and nickel, composite oxides of lithium and manganese. The cathode active substance can also be mixed with electroconductive substances (usually,
35 carbon) and a suitable amount of binder and is kneaded with a solvent to prepare a paste which is then applied to a collector (generally an aluminum collector) and is then dried and compacted to obtain the cathode.

The binders for cathodes can be the same than disclosed for the anodes and are preferably based on fluorinated resins.

For both types of electrodes, the amount of binder is generally of 1 to 30 parts, preferably 3 to 15 parts by weight, with respect to 100 parts by weight of electrode active substance.

But, as mentioned above, fluorinated resins, having inherently poor adhesion to metals, the electrode (active substance + binder) separate easily from the collector for both types of electrodes i.e cathode and anode, resulting in inferior cycle property of cells. JP5-6766 has proposed to roughen a surface of collectors to increase the anchoring effect of the fluorinated resins. However, sufficient adhesion cannot be achieved by this technique.

The present invention provides improved binders consisting of the above metal-adhesive compositions :

1/ which contains(a) and (b) only, the amount of (b) corresponding to 0.5 to 20 wt% of the total composition

2/ which contains(a) and (c) only, the amount of (c) corresponding to 0.5 to 50 wt% of the total composition,

3/ which contains(a) (b) and (c) only, the amount of (b) corresponding to 0.5 to 20 wt% of the total composition and the amount of (c) corresponding to 0.5 to 50 wt%.

The electrode can be produced by the steps of kneading predetermined amounts of electrode active substance and binder in the presence of solvent to obtain a slurry, coating the resulting slurry onto a collector of an electrode and drying the slurry, optionally followed by press-molding. The coated slurry is preferably subjected to heat-treatment at 60 to 250 °C, preferably 80 to 200 °C for 1 minute to 10 hours. The resulting band-shaped electrode can be wound together with separator sheet to produce a spirally wound cylindrical electrode.

The solvent used to prepare the slurry to be coated on a metal collector can be water and/or an organic solvent as N-methylpyrrolidone, N, N-dimethylformamide, tetrahydrofuran, dimethyl acetoamide, dimethyl sulfoxide, hexamethylsulfonamide, tetramethylurea, acetone and/or methylethyl ketone. Among these solvents, N-methylpyrrolidone is preferably used. If necessary, a dispersant can also be used, and preferably an nonionic dispersant.

Below, the present invention is explained by means of examples, but the invention is not to be restricted in any way by the said examples.

Example 1

100 parts by weight of PVDF resin pellets consisting of Kynar® 710, (sold by the applicant, melting point 170°C, MFR at 230°C/2.16kg load = 12g/10min), 30 parts by weight of polymethylmethacrylate in which maleic anhydride had been introduced as a copolymer component (Sumipex TR, made by Sumitomo Chemical Co.) and 70 parts by weight of hexafluoropropylene/vinylidene fluoride copolymer (Kynar® 2800 sold by the applicant, MFR at 230°C/12.5kg load = 6g/10min, melting point 142°C) were introduced into a blender and, after mixing, pellets were produced from the composition comprising these three components using a twin-screw extruder with the cylinder temperature set at 170-240°C.

Using a film (A) of thickness about 0.2mm produced from these pellets using a single-screw extruder, a separately-produced Kynar® 710 film (B) (of thickness 0.3mm), and a steel sheet (C) of thickness 1mm, these were superimposed in the order B/A/C and then pressing carried out for 10 minutes at 180°C at a maximum pressure of about 10kg/cm². After cooling to room temperature, a 2cm wide layer of B/A was stripped away from the steel sheet at 23°C using a tensile testing machine, at a rate of 100mm/min. When the force was measured, the adhesive strength was found to be 2.0kg/cm.

Example 2

Except for changing the proportions of Example 1 to 2 parts by weight of the Sumipex TR and 5 parts by weight of the Kynar 2800 per 100 parts by weight of the Kynar 710, pellets of the composition comprising these three components were produced by the same method as in Example 1. When the adhesive strength between the steel sheet and the PVDF resin layer was measured in the same way as in Example 1, it was 310g/cm.

Example 3

100 parts by weight of PVDF resin powder sold by the applicant under Kynar® 310F, melting point 160°C, MFR at 230°C/12.5kg load = 1.2g/10min), 1 part by weight of Sumipex TR and 1 part by weight of Kynar® 2800 were introduced into 1000ml of N-methylpyrrolidone, and a uniform solution obtained by stirring for about 24 hours at 30°C.

This solution was coated onto 1mm thickness copper sheet and aluminium sheet which had been degreased with toluene, and then the solution dried for 2 hours at 120°C. The thickness of the PVDF resin layer was about 50 µm. When the PVDF resin layer was cut at spacings of 1mm and a cross-cut adhesion test (based on Japanese standard JIS K5400, 6.15) and a tape peeling test carried out, in neither test was any separation of the PVDF resin layer noted.

Example 4

Excepting that, as the acrylic polymer with functional groups which exhibit good bonding properties or affinity in respect of metals in Example 3, there was used a copolymer of maleic anhydride, N-methyl-dimethylglutarimide, carboxylic-acid-containing monomer and methyl methacrylate (Paraloid® EXL4151 sold by Rohm and Haas), a solution of metal-adhesive composition was prepared in the same way as in Example 3. When the adhesive strength was measured in the same way as in Example 3, no peeling of the PVDF resin layer was noted and the adhesive strength was excellent.

Example 5

Excepting that, as the acrylic polymer with functional groups which exhibit bonding properties or affinity in respect of metals in Example 3, there was used polymethyl methacrylate to which epoxy-modified polymethyl methacrylate had been grafted (made by Toagosei Chemical Industry Co., Rezeda GP-301), a solution of metal-adhesive composition was prepared in the same way as in Example 3.

When the adhesive strength was measured in the same way as in Example 3, no peeling of the PVDF resin layer was noted and the adhesive strength was excellent.

Example 6

Using a co-extruder comprising a co-extrusion head for obtaining a two-layer thermoplastic structure and two extruders for supplying molten resin thereto (extruder A having a screw of compression ratio 3.5 and L/D = 15 and extruder B having a screw of compression ratio 4 and L/D = 20), PVDF resin sold by the applicant under Kynar®740) was extruded from extruder A and the adhesive composition obtained in Example 1 was extruded from extruder B, to produce a composite film comprising a 0.3mm PVDF resin layer and a 0.1mm adhesive layer. The cylinder temperatures of extruders A and B at this time were 170-240°C and 150-220°C respectively.

When the adhesive strength between the film obtained and steel sheet was measured by the same method as in Example 1, it was 1.9kg/cm.

Comparative Example 1

100 parts by weight of PVDF resin pellets Kynar ®710) and 30 parts by weight of a copolymer of maleic anhydride and methyl methacrylate (Sumipex TR sold by Sumitomo Chemical Co.,) were introduced into a blender and, after mixing together, there was produced a film of thickness about 0.1mm using a twin-screw extruder set at a cylinder temperature of 170-240°C.

When the adhesive strength in terms of steel sheet was measured by the above method, using this film and a separately-prepared Kynar®710 film (of thickness 0.3mm), the value was no more than 1kg/cm.

Comparative Example 2

- 5 100 parts by weight of PVDF resin powder (Kynar®301F) was dissolved in 1000ml of N-methylpyrrolidone and a solution produced. Then, in the same way as in Example 3, a PVDF resin layer was formed on metal sheet. When the adhesion properties were evaluated by means of a cross-cut adhesion test in the same way as in Example 3, it was found that, in the case of copper sheet, about 80% of the PVDF layer, and in the case of the aluminium sheet, all of the PVDF layer separated away due to the cutting at spacings of 1mm.

Comparative Example 3

- 15 100 parts by weight of Kynar®301F and 1 part by weight of Sumipex TR were dissolved in 1000ml of N-methylpyrrolidone, to produce a solution. When a PVDF resin layer was formed on aluminium sheet in the same way as in Example 3, and the adhesive strength measured, it was found that whereas in the cross-cut adhesion test about 80% of the PVDF layer remained without peeling, in the tape peeling test all the PVDF layer separated away.

Example 7

- 20 A binder solution was made by dissolving 10 parts by weight of polyvinylidene fluoride Kynar®500 and 0.1 part by weight of a methacrylate copolymer (MFR at 230 °C/3.8 kg : 2.4 g/10 min) comprising 100 parts by weight of methylmethacrylate and 10 parts by weight of maleic anhydride in N-methylpyrrolidone. Then, 90 parts by weight of coal pitch coke crushed in a ball mill as anode active substance was added to the solution to obtain a slurry (paste). The slurry was coated on both sides of a copper foil of thickness 20 µm, heated at 120 °C for 1 hour, dried under reduced pressure and then press-molded to obtain a cathode of thickness of 140 µm and of 20 mm.

A cathode was prepared as follows :

- 30 90 parts by weight of LiCoO₂ as cathode active substance, 6 parts of graphite as electro-conductive additive, 10 parts by weight of PVDF as binder and 0.1 part by weight of the above-mentioned methylmethacrylate-maleic anhydride copolymer were mixed and dispersed in N-methylpyrrolidone to obtain a slurry (paste). The slurry was coated on both sides of an aluminum foil of thickness 20 µm, heated at 120 °C for 1 hour, dried under reduced pressure and then press-molded to obtain anode having a thickness of 170 µm and of width 20 mm.

A good adhesion between the electrodes and the collectors was noted : the collectors cannot be removed from the surface of the electrodes when peeled off with a cutter-knife.

5 The resulting cathode and anode were laminated alternately through a film of porous polypropylene of thickness of 25 μm as separator to form a laminate of separator/cathode/separator/anode/separator which was wound up spirally to obtain a cylindrical electrode assembly. After lead wires were attached to respective electrodes, the electrode assembly was packed in a stainless container into which an electrolyte was poured. The electrolyte is 1 M solution of LiPF_6 dissolved in a
10 equivolumic mixture of propylene carbonate and 1, 2-dimethoxyethane.

A charge-discharge test was effected : the battery was charged with a current density of 30 mA / 1 g of carbon to 4.1 V and then was discharged with the same current to 2.5 V. The same charge-discharge operation was repeated to evaluate the capacity of discharge. The capacity of discharge after 100 cycles was 90 % of a
15 value of 10th cycle.

Example 8

The procedure of Example 7 was repeated but and the methacrylate copolymer was changed to a block copolymer consisting of methymethacrylate block and a copolymer block comprising methymethacrylate and acrylic acid (acrylic acid
20 contents 5 % by weight) and as the PVDF type resin, a copolymer of vinylidene fluoride and hexafluoropropylene sold by the applicant under Kynar ® 2800) was used to prepare both anode and cathode.

A good adhesion between the electrodes and the collectors was noted : the collectors cannot be removed from the surface of the electrodes when peeled off
25 with a cutter-knife.

A cell was manufactured by the same method as Example 1 and the same charge-discharge test was effected. The capacity of discharge after 100 cycles was 85 % of a value of 10th cycle.

Comparative Example 4

30 The same procedure as Example 7 was repeated but no methacrylate copolymer was added to the slurry during the preparation of both anode and cathode.

No part of collector remains on the electrode when peeled off with a cutter-knife.

35 A cell was manufactured by the same method as in Example 7 and the same charge-discharge test was effected. After 100 cycles the capacity of discharge was 50 % of a value of 10th cycle.

Example 9

A binder solution was made by dissolving 10 parts by weight of polyvinylidene fluoride Kynar ®500 and 0.3 parts by weight of a copolymer of vinylidene fluoride and hexafluoropropylene (contents of hexafluoropropylene: 10 %
5 by weight, a product of Elf Atochem, Kynar ®2820, MFR of 1.0 g/10 min at 230 °C under a load of 2.16 kg) in N-methylpyrrolidone. Then, 90 parts by weight of coal pitch coke crushed in a ball mill as anode active substance was added to the solution to obtain a slurry (paste). The slurry was coated on both sides of a copper foil of thickness 20 µm and whose surfaces have been roughened previously by
10 Emery paper No. 1000, heated at 120 °C for 1 hour, dried under reduced pressure and then press-molded to obtain a cathode of thickness of 140 µm and of width 20 mm.

A cathode was prepared as follows: 90 parts by weight of LiCoO₂ as cathode active substance, 6 parts of graphite as electro-conductive additive and 10 parts by
15 weight of the same PVDF and 0.3 % by weight of the same fluorinated copolymer as binder were mixed and dispersed in N-methylpyrrolidone to obtain a slurry (paste). The slurry was coated on both sides of the aluminum foil whose surface have been roughened previously by Emery paper No. 1000, heated at 120 °C for 1 hour, dried under reduced pressure and then press-molded to obtain anode of thickness 165 µm
20 and of width 20 mm.

A good adhesion between the electrodes and the collectors was noted : the collectors cannot be removed from the surface of the electrodes when peeled off with a cutter-knife.

The resulting cathode and anode were laminated alternately through a film of
25 porous polypropylene of thickness of 25 µm as separator to form a laminate of separator/cathode/separator/anode/separator which was wound spirally to obtain a cylindrical electrode assembly. After lead wires were attached to respective electrodes, the electrode assembly was packed in a stainless container into which an electrolyte was poured. The electrolyte is 1 M LiPF₆ solution dissolved in an
30 equivolumic mixture of propylene carbonate and 1, 2-dimethoxyethane.

In the charge-discharge test, the battery was charged with a current density of
30 mA / 1 g of carbon to 4.1 V and then was discharged with the same current to 2.5 V. The same charge-discharge operation was repeated to evaluate the capacity of discharge. The capacity of discharge after 100 cycles was 90 % of a value of 10th
35 cycle.

Example 10

The procedure of Example 9 was repeated but the vinylidene fluoride copolymer was changed to a copolymer of vinylidene fluoride and tetrafluoroethylene (Kynar ® 2820, weight contents of tetrafluoroethylene : 27 %, MFR of 3 g/10 min at 230 °C under a load of 2.16 kg) to prepare an anode and a cathode.

A good adhesion between the electrodes and the collectors was noted : the collectors cannot be removed from the surface of the electrodes when peeled off with a cutter-knife.

A cell was manufactured by the same method as Example 9 and the same charge-discharge test was effected. The capacity of discharge after 100 cycles was 85 % of a value of 10th cycle.

Comparative Example 5

The procedure of Example 9 was repeated but no vinylidene fluoride copolymer was added to the slurry for electrodes.

No part of both collectors remains on both electrodes when peeled off with a cutter-knife.

A cell was manufactured by the same method as in Example 9 and the same charge-discharge test was effected. After 100 cycles the capacity of discharge was 60 % of a value of 10th cycle.

Example 11

A binder solution was made by dissolving 10 parts by weight of PVDF Kynar 500, 0.1 part by weight of a methacrylate copolymer (melt flow index of 2.4 g/10 min at 230 °C under a load of 3.8 kg) comprising 100 parts by weight of methylmethacrylate and 10 parts by weight of maleic anhydride, and 0.1 part by weight of a copolymer of vinylidene fluoride and hexafluoropropylene Kynar®2800 MFR of 0.2 g/10 min at 230 °C under a load of 2.16 kg) in N-methylpyrrolidone. Then, 90 parts by weight of coal pitch coke crushed in a ball mill as anode active carrier was added to the solution to obtain a slurry (paste). The slurry was coated on both sides of a copper foil of thickness 20 µm, heated at 120 °C for 1 hour, dried under reduced pressure and then press-molded to obtain an anode of thickness 145 µm and of width 20 mm.

A cathode was prepared as follows: 90 parts by weight of LiCoO₂ as cathode active substance, 6 parts of graphite as electro-conductive additive, 10 parts by weight of PVDF, 0.1 part by weight of the above-mentioned methacrylate copolymer and 0.1 part by weight of the above copolymer of vinylidene fluoride and hexafluoropropylene as binder were mixed and dispersed in N-methylpyrrolidone to obtain a slurry (paste). The slurry was coated on both sides of an aluminum foil of

thickness 20 μm , heated at 120 $^{\circ}\text{C}$ for 1 hour, dried under reduced pressure and then press-molded to obtain an anode of thickness 175 μm and of width 20 mm.

A good adhesion between the electrodes and the collectors was noted : the collectors cannot be removed from the surface of the electrodes when peeled off with a cutter-knife.

The resulting cathode and anode were laminated alternately through a film of porous polypropylene of thickness 25 μm as separator to form a laminate of separator/cathode/separator/anode/separator which was wound up spirally to obtain a cylindrical electrode assembly. After lead wires were attached to respective electrodes, the electrode assembly was packed in a stainless container into which an electrolyte was poured. The electrolyte is 1 M solution of LiPF_6 dissolved in an equivolumic mixture of propylene carbonate and 1, 2-dimethoxyethane.

In the charge-discharge test, the battery was charged with a current density of 30 mA / 1 g of carbon to 4.1 V and then was discharged with the same current to 2.5 V. The same charge-discharge operation was repeated to evaluate the capacity of discharge. The capacity of discharge after 100 cycles was 95 % of a value of 10th cycle.

Example 12

The procedure of Example 11 was repeated but the methacrylate copolymer was replaced to a block copolymer consisting of methylmethacrylate block and a copolymer block comprising methylmethacrylate and acrylic acid (weight contents of acrylic acid : 5 %) and the fluorinated copolymer was replaced by a copolymer of vinylidene fluoride and tetrafluoroethylene (weight contents of tetrafluoroethylene : 27 %, MFR of 3 g/10 min at 230 $^{\circ}\text{C}$ under a load of 2.16 kg) to prepare an anode and a cathode.

A good adhesion between the electrodes and the collectors was noted : the collectors cannot be removed from the surface of the electrodes when peeled off with a cutter-knife.

A cell was manufactured by the same method as Example 11 and the same charge-discharge test was effected. The capacity of discharge after 100 cycles was 92 % of a value of 10th cycle.

Comparative Example 6

The same procedure as Example 1 was repeated but the methacrylate copolymer and the fluorinated copolymer were not added to the slurry in preparation of both anode and cathode.

No part of both collectors remains on both electrodes when peeled off with a cutter-knife.

A cell was manufactured by the same method as in Example 11 and the same charge-discharge test was effected. After 100 cycles the capacity of discharge was 50 % of a value of 10th cycle.

Claims

1. Metal-adhesive fluorinated composition comprising at least 2 of the 3 following components :
 - (a) at least a PVDF resin,
 - 5 (b) at least a acrylic an/or methacrylic polymer having functional groups with bonding properties or affinity in respect of metals,
 - (c) at least a vinylidene fluoride copolymer resin.
2. Composition according to claim 1 containing from 0.5 to 100 parts by weight of an acrylic and/or methacrylic polymer (b), from 1 to 200 parts by weight of
10 vinylidene fluoride copolymer resin (c) per 100 parts by weight of polyvinylidene fluoride resin (a).
3. Method for the adhesion of fluorinated resins to metals, characterized in that the composition as defined in claim 1 or 2 is carried out as adhesive agent between the fluorinated resins and the metals.
- 15 4. Method for the adhesion of fluorinated resins to metals, characterized in that the fluorinated resins to be coated to the metals is replaced by any one of the compositions as defined in claim 1 or 2.
5. Electrode's binder made of a composition as defined in claim 1 and which contains (a) and (b) only, the amount of (b) corresponding to 0.5 to 20 wt% of
20 the total composition of the binder.
6. Electrode's binder made of a composition as defined in claim 1 and which contains (a) and (c) only, the amount of (c) corresponding to 0.5 to 50 wt% of the total composition of the binder.
7. Electrode's binder made of a composition as defined in claim 1 or 2
25 and which contains (a) (b) and (c) only, the amount of (b) corresponding to 0.5 to 20 wt% of the total composition of the binder and the amount of (c) corresponding to 0.5 to 50 wt%.
8. Electrode comprising a metallic collector coated on the electrode comprising an active substance and a binder according to claim 5 to 7.
- 30 9. Battery and/or cell comprising at least one electrode as defined in claim 8, and preferably lithium-ion battery and/or cell.

INTERNATIONAL SEARCH REPORT

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 03 213 336 A (MITSUBISHI PETROCHEM. CO., LTD.) 18 September 1991 & CHEMICAL ABSTRACTS, vol. 116, no. 2, 13 January 1992 Columbus, Ohio, US; abstract no. 7659, see abstract ---	1-4
X	DE 20 22 279 A (DAIKIN KOGYO CO., LTD) 19 November 1970 see claims; examples 8-14 ---	1-4
P,A	JP 08 088 385 A (FUJI ELECTRIC CORP. RES. & DEV., LTD.) 2 April 1996 & DATABASE WPI Derwent Publications Ltd., London, GB; AN 96-227546 see abstract ---	1
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 601 754 A (KUREHA CHEMICAL IND CO LTD) 15 June 1994 see claims -----	1,5

INTERNATIONAL SEARCH REPORT

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International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 03213336 A	18-09-91	NONE	
DE 2022279 A	19-11-70	FR 2047421 A GB 1313701 A US 3773713 A	12-03-71 18-04-73 20-11-73
JP 08088385 A	02-04-96	NONE	
EP 0601754 A	15-06-94	JP 6172452 A CA 2110314 A US 5415958 A	21-06-94 03-06-94 16-05-95

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(54) Title: METHOD FOR THE ADHESION OF FLUORINATED RESINS TO METALS

(57) Abstract

The objective of the present invention is to offer a method for improving the adhesion of fluorinated resins to metal materials, and for obtaining composite materials of metal materials and polyvinylidene fluoride resins. A metal-adhesive fluorinated composition can be used as an adhesive agent between the fluorinated resins and the metals or can replace the fluorinated resins.

* (Referred to in PCT Gazette No. 45/1997, Section II)

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INTERNATIONAL SEARCH REPORT

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